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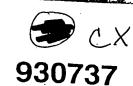
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David R. Monroe, Craig L. DiMaggio, Donald D. Beck, and Frederic A. Matekunas General Motors Research Labs.

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Evaluation of a Cu/Zeolite Catalyst to Remove NO_x from Lean Exhaust

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ABSTRACT

A Cu/ZSM-5 catalyst has been tested in both the laboratory and in a gasoline-fueled, lean-burn car. This catalyst is generally believed to be the current "state of the art" for removing NO_X from lean engine exhaust. The laboratory tests showed that the HC species was the exhaust component which reduced the NOx. This catalyst actually produced CO, but the CO had no impact on the NO_x reduction. The NO_x conversion was inhibited by oxygen at oxygen levels below 4%, but was also modestly inhibited by oxygen levels above 4%. The NO_X conversion of these catalysts was less affected by SO₂ than were the HC and CO conversions. These catalysts showed very poor thermal durability, losing much of their activity after aging under conditions milder than those typically used for three-way catalysts.

The vehicle tests of the fresh Cu/ZSM-5 catalyst showed between 30 and 40% average $NO_{\rm X}$ conversion. Hence, the car on which this catalyst was tested would have to have engine-out $NO_{\rm X}$ emissions of less than 0.65 g/ml in order to meet a 0.4 g $NO_{\rm X}$ /ml talipipe standard, the most lenient of the 1996 Federal emission standards. Since this catalyst had very poor HC performance, it is likely that it would be difficult to meet the future HC standards if this catalyst were used alone. The durability of the lean $NO_{\rm X}$ catalyst must also be improved.

INTRODUCTION

Virtually all of the new gasoline-fueled vehicles sold in the United States today operate with a stoichiometric mixture of air and fuel, then use a three-way catalyst to reduce the hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO_X) emissions. With existing technology, the efficient simultaneous reduction of all

three of these regulated emission species requires that the exhaust stoichiometry be maintained very close to the stoichiometric point. However, it is known that these engines would get better fuel economy if they could operate lean of the stoichiometric point. In this lean mixture, many catalysts are very effective in oxidizing the HC's and CO but are ineffective in reducing the NO_x.

Thus, many research programs over the last fifteen years have been directed at either reducing the engine-out NO_X emissions from lean-burn engines or at finding a catalyst which would reduce NO_X in lean exhaust.

The engine-out emissions from a gasoline fueled car depend on many factors, but are generally in the 4 g NO_X /mi domain when no efforts are taken to reduce them. Using exhaust gas recirculation (EGR) to dilute the charge to the engine brings the engine-out NO_X level down to the range of 2 g NO_X /mi. Similarly, air can be used to dilute the charge to the engine, easily bringing the engine-out NO_X level below 2 g/mi. The current state-of-the-art in lean-burn systems has brought the engine-out NO_X to about 1 g NO_X /mi, currently the maximum allowable NO_X emission level. At this level it is not viable for production and is well above the highest of the 1996 NO_X regulations (0.4 g NO_X /mi).

There is some evidence in the patent literature of the use of zeolite materials to remove NO_X from lean exhaust as far back as 1974 (1, 2), but these results received little attention. The interest in zeolites was accelerated with the independent publication of results by Held (3) and Iwamoto (4) indicating that Cu-impregnated zeolites had reasonable lean NO_X activity. Held demonstrated that lean NO_X conversions as high as 45% could be obtained using a Cu/ZSM-5 catalyst to

treat the exhaust of a lean-burn gasoline engine. Iwamoto showed that these catalysts have a temperature window at about 500°C where they operate best. Both Iwamoto and Held showed that hydrocarbons present in the feed are the main species which reduce the NO_X.

Many different metals and many different zeolite structures have been investigated in the last several years (5,8) but none has been found which is superior to the Cu/ZSM-5 system. The most promising of the alternatives is a cobalt based system, but this needs higher temperatures to operate than do the Cu based systems. Recently, attention has also been focused on trying to develop silica aluminum phosphate based zeolites with the hope that they may have improved pore structures and better hydrothermal durability, but results on these systems are not yet available (7).

The work presented in this report was undertaken to assess the ability of a current state-of-the-art Cu/ZSM-5 lean NO_{X} catalyst to reduce NO_{X} in the exhaust from a lean-burn car that is also state-of-the-art.

EXPERIMENTAL

Three monolithic biscuits were washcoated with Cucontaining ZSM-5 zeolite by Johnson Matthey for this study. All three biscuits were standard GM race-track monoliths (major axis 18.5 cm, minor axis 8 cm) with 62.2 channels/cm² (400 channels/in²). One of the biscuits was 15.2 cm long, while the remaining 2 were 12.7 cm long. One of the shorter biscuits and the longer biscuit were placed in a standard GM model 170 converter canister that had been modified to be taken apart. The remaining biscuit was cut apart to provide samples 1.27cm x 1.27 cm wide by 2.54 cm long for testing in the laboratory reactor.

The zeolite material was purchased from the PQ corporation and was a high Al:Si (=70:1) ZSM-5 zeolite. The zeolite was ion exchanged with a Cu-containing sait until it contained 3.2 wt % copper. The Cu-containing zeolite was mixed with alumina, reducing the Cu content of the washcoat to 2.7%. The washcoat was coated onto the monolithic substrates to give a Cu loading of 90 gyft3.

The laboratory evaluations of these catalysts were performed in a quartz reactor operating with blended gases. The reactor consisted of a 2.5 cm ID quartz tube surrounded by a tube furnace. The catalytic material was placed directly at the outlet from the heated zone of the reactor. This reactor has been described in great detail in a previous publication (8). The gases to the reactor were blended to be similar in composition to the average composition from the lean-burn car during the first phase of an FTP test. The

exhaust composition and the average first phase exhaust composition are shown in Table 1. The space velocity used in the reactor was almost thre times higher than that in the car because this was the lowest flow rate at which the reactor could be operated.

Table 1
Comparison of Typical reactor Feed and Engine-Out
Emissions from Lean-Burn Car

Laborato Reacto		Lean- Burn Car		
7	% O ₂	6.3		
800	ppm Propylene	700		
200	ppm NO _v	240		
0.2	% CO 1			
10	% H ₂ O	0.2		
10	70 1120	9		
	% CŌ ₂	9		
. 0	ppm SO2	15		
	Space			
45 000	Mala-14 . 4	18 000		

In all of the tests presented in this report, the flow was first adjusted to give the desired composition. The catalyst was then heated from a low temperature (< 200°C) to 600°C at a rate of 5°C/min. It was allowed to cool from the 600°C, again at a rate of 5°C/min. While the converter performance was monitored during both the heating and cooling portion of the test, only the data taken during the cooling portion was used. It was believed that the data taken during the cooling cycle would be more representative of the intrinsic kinetics reactions of the hydrocarbons stored on the support from the previous cooler section of the test.

The car used in the vehicle tests was an Oldsmobile Cutlass Clerra (GVW = 3250 lbs, or 1478 kg) with a 2.3-L engine. The cylinder head had two intake valves and a single exhaust valve per cylinder instead of two of each in the production head. The extra space achieved by the removal of the second exhaust valve provided space for a second spark plug for each cylinder. This dual spark plug configuration along with the ability to throttle one of the inlet valves allowed the engine to operate leaner than would have otherwise been possible. The engine was controlled by monitoring the cylinder pressures, providing information for the control of both fueling and spark timing. The engine operated with constant charge dilution, hence under high flow conditions where there was less internal EGR, there was more air and a higher A/F. Once the engine was warm, it operated in an A/F range of from 17:1 to 23:1.

The vehicle was tested on a chassis dynamometer in the RES Vehicle Emissions Laboratory. The exhaust was sampled before and after the converter and analyzed by two sets of Horiba analyzers scanned at 2 Hz. The development control system did not have a well calibrated cold start, hence, the first 18 cycles of the urban FTP schedule were run from a warm idle as an initial condition for the evaluation of the converter performance. Indolene fuel was used for these tests. The NO_X analyzers were operated in the NO mode in order to maximize their time response.

RESULTS AND DISCUSSION

LABORATORY RESULTS

Effect of Temperature

The HC, CO, and NO_x conversions of the Cu/ZSM-5 catalyst are shown in Figure 1 using the standard feed (Table 1) as the catalyst was cooled from 600 to 100°C. The HC conversion behaves in the same manner as it would for a Cu-Al₂O₃ catalyst; the conversion is initially very low at low temperatures, has a gradual lightoff in the 350-450°C range, and increases further as the temperature increases (9). The behavior of the NO_X conversion is similar to that of the HC conversion at temperatures below 450°C, only it is shifted to ≈50°C higher temperatures. The NO_X conversion differs from that of hydrocarbons at temperatures above 450°C. The rate of increase in the NO_X conversion first begins to slow, with the NO_X conversion then reaching a maximum of 42% at 500°C. The NO_X conversion then decreases as the temperature increases further. This is similar to the behavior of fresh noble metal catalysts in lean exhaust where NO_X conversion is seen to peak, frequently in the 50-60% range, in the temperature domain where the catalyst is reaching 50% HC and CO conversions, then decreases as the HC and CO conversions increase. The CO conversion of the Cu/ZSM-5 catalyst was unique. The CO conversion was initially low, as would be expected. But instead of increasing as the HC conversion increased, the CO conversion actually decreased. The CO conversion was negative between 420 and 450°C idicating that the catalyst was producing CO. The CO conversion rose rapidly above 450°C.

This experiment was repeated without any CO in the feed in order to verify that the catalyst produces CO under some operating conditions and to determine the role of CO in reducing NO_x . These results are shown in Figure 2. The HC and NO_x conversions were very

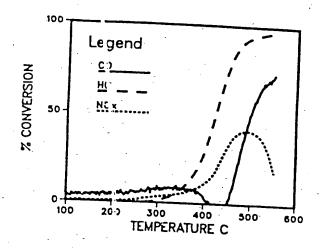


Figure 1. HC, C(), and NO_X conversions as a function of temperature a: the catalyst is cooled for a fresh Cu/ZSM-5 catalyst. Feed is standard feed defined in Table 1.

similar to what was observed in the previous run, indicating that the HC species was much more important than CO in reducing NO_X. This experiment also clearly showed the tendency of the Cu/ZSM-5 catalyst to produce CO at temperatures above 350°C. Between 450 and 550°C ~25% of the HC in the feed was turned into CO.

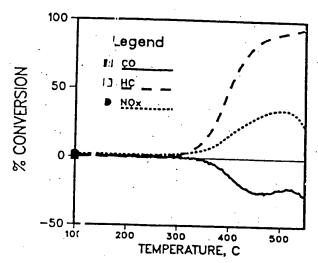


Figure 2. HC, CO, and NO_x conversions as a function of temperature as the catalyst is cooled. The feed was the standard feed (Table 1) only with no CO. The % CO conversion is defined as minus the % of the HC conversion which formed CO.

Effect of Oxygen Concentration

The cool-down experiments were repeated using the standard feed except for oxygen, which was varied from 2 to 10%. All of these feeds were highly net oxidizing, as a stoichiometric oxygen concentration was 0.45% oxygen. The maximum NO_X conversion was determined for each feed (it usually occurred very close to 500°C) and is plotted in Figure 3 as a function of the oxygen concentration. The lowest NO_x conversion was found at 2% oxygen, while the second lowest was found at 8% oxygen. Though there is obviously a lot of scatter in the results, the results are compatible with previous reports showing very poor NO_X conversions at low oxygen concentrations, a maximum NO_X conversion in the 2-4% oxygen range, and moderate inhibition by oxygen at higher concentrations (5,6,7).

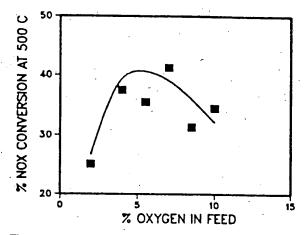


Figure 3. NO_X conversion as a function of oxygen concentration as the catalyst is cooled. The feed was the standard feed (Table 1) except for the oxygen concentration.

Effect of Hydrocarbon Concentration

Experiments similar to those performed investigating the effect of the oxygen concentration were repeated only varying the HC concentration instead of the oxygen concentration. The HC (propylene) concentration was varied from 200 ppm to 1000 ppm, giving HC:NO $_{\rm X}$ ratios of from 3:1 to 15:1 (based on a C $_{\rm 1}$ basis). The maximum NO $_{\rm X}$ conversion which was obtained in each run is plotted in Figure 4 as a function of the feed HC concentration. The results show that the NO $_{\rm X}$ conversion increases markedly as the HC concentration increases, as would be expected from the previous results which indicated that the NO $_{\rm X}$ was being reduced by HC rather than by CO. The NO $_{\rm X}$ conversion dependence is also in agreement with previous work (3,4,5).

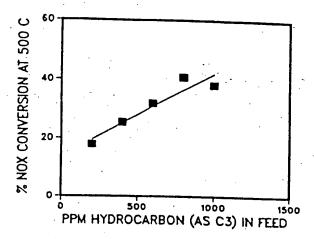


Figure 4. NO_X conversion as a function of hydrocarbon concentration as the catalyst is cooled. The feed was the standard feed (Table 1) except for the oxygen concentration.

Effect of Space Velocity

The reactor feed rate was increased from the standard rate of 3 L/min (S.V. of 45 000 h⁻¹) to 8 L/min (S.V. of 120 000 h⁻¹) in order to determine the effect of the space velocity on the conversion efficiency of the converters. The results are listed in Table 2.

Table 2
Effect of Space Velocity on the 500°C Conversion
Efficiency of
Cu/ZSM-5 Catalyst at Standard Feed Composition

	Space	• Velocity, h ⁻¹
	45 000	120 000
HC	95%	83%
CO	51%	26%
NOX	41%	38%

The HC conversion fell from 95% to 83% when the space velocity increased. This was not surprising, though it would have been anticipated that the HC conversion would fall to 68% had the rate of HC oxidation been first order with respect to the HC concentration. The marked reduction in the CO conversion efficiency could also have been anticipated, since only a slight shift in the conversion as a function of temperature can result in a large change in the conversion at 500°C (see Figure 1).

While there were large reductions in the conversion efficiencies of HC and CO, there was only a modest

reduction in the NO_X conversion as it fell from 41 to 38%. This was not expected in that it was thought that the NO_X reduction was a slow reaction and would thus show a very strong dependency on the space velocity. The lack of dependency can, perhaps, be explained in part by the HC conversion. The HC concentration was 3.6 times higher at the outlet of the reactor at the high space velocity than at the slower space velocity, hence providing a means of accelerating the NO_X reduction and largely offsetting the almost three-fold difference in the space velocities.

Effect of SO2 .

All of the previously discussed tests were performed in the absence of SO₂. The last test which was performed on the fresh Cu/ZSM-5 sample was to add 20 ppm of SO₂ to the feed. This test was performed after the others so that there would be no repeatability problem arising from irreversible sulfur poisoning. The conversion efficiencies with 5 and 20 ppm of SO₂ in the feed as well as the conversion efficiencies before exposure to SO₂ are listed in Table 3.

Table 3
Effect of SO₂ Concentration on the 500°C Conversion
Efficiency of Cu/ZSM-5 Catalyst

	SO_2	Concentration	, ppm
	0 _	5	20
HC	95	85	81
CO	51		
NOx	41	36	36

The SO_2 reduced the HC conversion efficiency, in agreement with many previous studies using Al_2O_3 supports (ref. 9, for example). The warrned-up CO conversion became negative upon the addition of the SO_2 , indicating that these catalysts are again producing CO. The NO_{χ} conversion also fell upon the addition of the SO_2 , but only by 5%. This may be a situation similar to that with the space velocity; the negative impact of the SO_2 on the NO_{χ} conversion rate may be largely offset by an acceleration of the rate by the higher HC concentration within the catalyst.

Catalyst Durability

The durability of the Cu/ZSM-5 catalyst was investigated by aging samples of the catalyst in three environments: 800° C for 4 h in a 5% H_2/N_2 feed; 800° C for 4 h in a 5% O_2/N_2 feed; and 800° C for 4 h in a feed that was switched between 5% H_2/N_2 and 5% O_2/N_2 every 10 s. These conditions are not as severe

as the 1000°C aging temperatures usually used to simulate the aging of three-way catalysts.

The HC, CO, and ${\rm NO_X}$ conversions at 500°C during cool-down experiments are listed in Table 4.

Table 4
Effect of Thermal Aging on the 500°C Conversion
Efficiency of
Cu/ZSM-5 Catalyst Aged at 800°C for 4h

	Agin	g Environm	ent	•
	Fresh	5% O2	5% H2	Cycled
HC	94 -	75	71	- 74
CO	51	••	77	47
NOX	41	14	. 8	9

The thermal aging reduced the HC conversion efficiency of these catalysts, independent of the gas environment. The CO conversion increased following the aging in H₂, was only slightly lower following the cyclic aging, and the catalyst was a net producer of CO at 500° C following aging in O₂. All three of these gas environments severely degraded the NO_X conversion efficiency at 500° C.

Some insight into the aging process of these catalysts can be gained by examining the full temperature dependency of these catalysts and comparing them to the fresh sample. The catalyst aged in the hydrogen and the catalyst aged in the cycled feed were, except for CO, very similar so only the hydrogen aged catalyst will be discussed. Figure 5 shows the HC, CO, and NO_X conversions for the hydrogen aged catalyst as a function of temperature as it was cooled from $500^{\circ}C$.

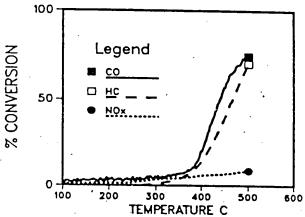


Figure 5. HC, CO, and NO_X conversions as a function of temperature as the catalyst is cooled for a Cu/ZSM-5 catalyst aged at 800° C for 4 h in 5% H₂. Feed is standard feed defined in Table 1.

Of particular interest is that the HC and CO conversions follow one another as they begin to rise in the 400°C range. This is similar to what has been observed on base metal on Al₂O₃ catalysts (9). It differs markedly, though, from the fresh Cu/ZSM-5 catalyst in which the HC conversion begins to increase around 400°C, while the CO conversion decreases and actually goes negative in this temperature domain. The NO_x conversion of the catalyst aged in H2 remained very low throughout the test and it is possible that much of the 8% conversion seen at 500°C may be due to baseline drift. The catalyst which was aged in O2 showed almost the same HC conversion behavior as the sample aged in H2. The CO conversion, though, continued to exhibit a declining conversion around 400°C and became negative at 450 $^{\circ}$ C. The NO $_{\chi}$ conversion clearly increased above 400°C and appeared to be reaching a maximum at 500°C. Hence, while the Cu/ZSM-5 catalyst aged in H2 behaved like a classical base metal catalyst, the Cu/ZSM-5 catalyst aged in oxygen continued to behave as a zeolite supported catalyst, only at a level of NO_x activity significantly below that of the fresh catalyst.

The catalysts aged in the cycled feed and in the $\rm H_2$ feed both changed from white in color to a deep reddish brown, probably due to the formation of either Cu or Cu₂O crystallites. It is known that copper can easily be reduced to copper metal under reducing conditions and that in the metallic state it is mobile and can move out of the zeolite cages. This could then explain why the catalysts aged under reducing conditions no longer show the zeolite-like behavior.

VEHICLE TESTS

Two 18 cycle FTP tests were performed using the Cu/ZSM-5 catalyst in a modified Cutlass Cierra (see Experimental section). The emissions from these tests are listed in Table 5.

Table 5						
18	Cycle	Summary				

Avg. A/F	нс	CO g/ml	NOx	MPG
Hot Catalyst (250°C)		-		
Engine-Out 21,4	4.7	2.9	1.0	26.3
Converter-Out	1.6	3.7	0.6	
% Conversion	67	-25	40	
Warm Catalyst (120°C)				
Engine-Out 21.1	4.2	2.9	1.0	26.8
Converter-Out	2.1	3.7	0.7	
% Conversion	49	-29	30	

The air/fuel ratio reported in this table is the average over the cycle. Since the control system maintains relatively constant cliution, the A/F varied from about 17:1 at idle to almost 23:1 at wide-open throttle. The engine provided sufficient power to drive the test without enrichment.

The difference between the emissions from the hot and warm catalysts is a reflection of the longer time required for the warm catalyst to reach a temperature at which it can operate. The HC emissions were well above the current standard (0.41 g/ml) on both tests, while the CO was somewhat above the current standard (3.4 g/ml) on the two tests. The engine-out NO_x emissions were 1.0 g/ml, the same as the existing NO_x standard. The lean NO_x catalyst brought this down to the 0.6-0.7 g/ml range, well below the current standard but also well above the future standard of 0.4 g/ml.

The test with the warm catalyst was repeated with the NO_x analyzer in the NO_x mode and the results were similar to the previous test with the analyzer in the NO_x mode, indicating that N_2 was the dominant product from the NO_x reduction.

Modeling of Vehicle Tests

The data from the first 505 s of one of these tests (the first 505 s constitutes the first phase or "bag" of an FTP test) was analyzed to determine the cause for the variation in the NO_X conversion through the test. Figure 6 shows the NO_X conversion as a function of time for the first phase of an FTP test. The NO_X conversion efficiency of the Cu/ZSM-5 catalyst varied from over 80% to below zero. The conversions below zero are not

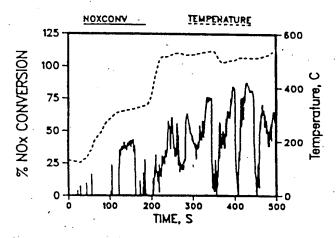


Figure 6. Temperature and NO_X conversion as a function of time for the first 5 cycles of a "Hot 18" cycle FTP test. Test vehicle is a Cutlass Clerra with a highly modified lean-burn 2.3 L engine.

shown in Figure 6 and probably represent errors in synchronizing the inlet and outlet meters rather than NO_x formation. Since temperature is expected to affect the NOx conversion, especially in the first phase, this figure also shows the bed temperature for the catalyst. The temperature is initially low, but well above ambient since this is a "Hot 18 Cycle" FTP test. The NO_{χ} conversion is low until about 120 s into the test at which time the NO_x conversion rises to a sustained 40%. This occurs when the converter is slightly above 300°C and during a period in which the car was at idle. The NO_X conversions were very erratic for the remainder of the first phase. The temperature rose rapidly at 180 s into the test, a time at which the car is in a rapid The converter temperature ranges acceleration. between 480 and 540°C for the remainder of the first phase. Further consideration of this data examined the period between 217 and 505 s since the temperature remained sufficiently high (between 480 and 540°C) for this period and could, at least as a first approximation, be ignored

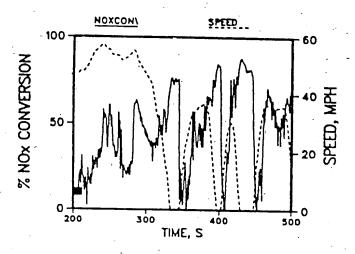


Figure 7. Vehicle speed and NO_x conversion as a function of time for the time period 217s to 505 s during a "Hot 18" cycle FTP test. Test vehicle is a Cutlass Clerra with a highly modified 2.3 L engine.

As an initial attempt to determine the factors that affected the NO_X conversion efficiency, the NO_X emissions were correlated against several parameters. Among those were: the moles of NO_X emitted, the NO_X concentration leaving the converter, the NO_X conversion efficiency, and the log of one minus the conversion efficiency. The last parameter corresponds to the form expected for a reaction rate that is first order with respect to the NO_X concentration. The correlation coefficients are listed in Table 6, as well as some of the average conditions for the first phase of the FTP test.

The negative correlation coefficients shown in this table indicate that the dependent variable decreased when the independent variable increased.

The moles of NO_{χ} (or mass) in the tailpipe exhaust were most closely correlated to the engine-out NO_{χ} level. The tailpipe NO_X conc ntration correlates most closely to the exhaust flow rate. The high correlation coefficient observed here (0.91) is probably a result of factors working together: the inlet NO_x concentration decreases as the flow rate decreases, and the conversion efficiency of the catalyst increases as the flow rate decreases. The NO_{χ} conversion showed a strong dependency on the engine-out NO_x concentration, the speed, the oxygen concentration and the flow rate. The A/F, oxygen concentration and residence time in the converter all had high correlation coefficients with log(1-Conv). However, all three of these are related to one another. As the air flow rate into the engine increases, the amount of internal EGR decreases and the A/F and oxygen concentration both increase while the exhaust residence time in the converter decreases.

A visual examination of the vehicle results supports the conclusion that the $\rm NO_X$ conversion is closely tied to the flow rate through the converter. Figure 7 shows both the speed and the $\rm NO_X$ conversion for the time when the catalyst is above 480°C. Note that the $\rm NO_X$ conversion is highest during the periods when the car is either decelerating or idling and that the $\rm NO_X$ conversion falls markedly when the car is accelerating. Both the deceleration and idle periods are associated with low exhaust flow rates, while the highest exhaust flow rates occur during periods of high engine output such as accelerations.

The warmed-up NO_X conversion was modeled assuming that the reaction was first order with respect to NO_X and zero order with respect to the HC concentration. The reaction rate constant for this was fit to the vehicle data using a least-squares minimization. The fit and the measured NO_X conversion are shown in Figure 8.

The model provides a reasonable approximation of the converter performance even though it is a relatively simple representation of what is probably a very complicated set of kinetics. Attempts to improve the fit of the model by including the effect of HC's and oxygen did not significantly improve the quality of the fit.

Table 6
Correlation Coefficients T > 480°C, 217 - 505 s

*	NO	A/F	Speed	HC	НС			
14	Eng-Out			Tallpipe	HC EngOut	02	Resid.	Exh.
Mean	235	20.5	50	228	705	6.4	Time 54	Flow
	ppm	·	km/h	ppm	ppm.	%	ms	176 9/8
Moles NO _x	0.70	0.51	0.53	0.56	-0.22	0.48	-0.56	0.63
NO _¥	0.78	0.79	0.37	0.76	-0.23	0.75	-0.71	0.91
Conv.	-0.87	-0.39	-0.83	-0.43	0.68	-0.81	0.75	-0.80
Log(1- conv.)	0.31	0.84	0.55	0.64	0.39	0.83	0.80	0.74

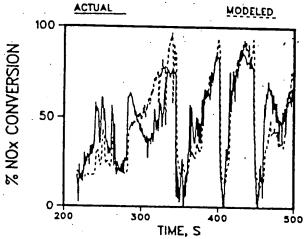


Figure 8. NO_X and modeled NO_X conversions as a function of time for the time period of 217s to 505 s during a "Hot 18" FTP test. Model is a one parameter fit to the data assuming that the reaction rate is first order with respect to NO_X .

CONCLUSIONS

Tests on an Oldsmobile Cutlass Clerra with a highly modified 2.3 L gasoline-fueled engine operating at a 20 - 22 A/F ratio showed average NO_X conversions in the 30 - 40 % range when tested with a fresh Cu/ZSM-5 catalyst. Conversions in this range would require engine-out emissions of less than 0.65 g NO_X/mi in order to meet the most lenient of the 1996 Federal emission standards, assuming no catalyst deterioration for 100 000 miles.

- Laboratory tests showed severe catalyst deterioration after aging at 800°C for 4 h. These are considered very mild aging conditions for three-way catalysts.
- 3. The Cu/ZSM-5 catalyst averaged between 50 and 70% HC conversion efficiency during vehicle tests. Meeting even the current HC emission standards would require a noble metal converter following the lean NO_x catalyst. However, since the lean NO_x catalyst must be closer to the engine than the noble metal catalyst, meeting even the most lenient of the future HC emission standards would probably require that external heat be supplied to the noble metal catalyst.
- 4. Vehicle tests of the Cu/ZSM-5 catalyst showed that it produced more CO than it converted (net CO production of ~25%), though CO emissions are not thought to be a problem for lean-burn cars operating with a lean NO_x catalyst. This is because the engine-out CO levels are quite low and the noble metal catalyst required for the HC emissions would easily remove most of the CO under these lean conditions. The formation of CO by the lean NO_x catalysts in the car is consistent with laboratory observations.
- 5. The vehicle tests revealed that the NO_X conversion from the warmed-up catalyst varies from 5 to 80%. Most of this variation appears to be a result of changing flow rates. However, the effect of the flow rate could not be separated from the effect of the oxygen concentration since both are related to one another.

6. In laboratory studies of a fresh Cu/ZSM-5 catalyst, NO_X conversion was found to have a maximum at ~500°C and was inhibited by oxygen levels above 4%. The conversion also fell as the flow rate increased and as the HC concentration decreased.

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